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CEMENTITIOUS BARRIERS PARTNERSHIP
FY2015 MID-YEAR STATUS REPORT

CBP-TR-2015-010, Rev. 0
CEMENTITIOUS BARRIERS PARTNERSHIP
FY2015 MID-YEAR STATUS REPORT

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FOREWORD

The Cementitious Barriers Partnership (CBP) Project is a multi-disciplinary, multi-institutional collaboration supported by the United States Department of Energy (US DOE) Office of Tank Waste Management. The objective of the CBP project is to develop a set of tools to improve understanding and prediction of the long-term structural, hydraulic, and chemical performance of cementitious barriers used in nuclear applications.

A multi-disciplinary partnership of federal, academic, private sector, and international expertise has been formed to accomplish the project objective. In addition to the US DOE, the CBP CRADA partners are the Savannah River National Laboratory (SRNL), Vanderbilt University (VU) (funded by the Consortium for Risk Evaluation with Stakeholder Participation (CRES)), Energy Research Center of the Netherlands (ECN), and SIMCO Technologies, Inc. The Nuclear Regulatory Commission (NRC) is providing support under a Memorandum of Understanding. The National Institute of Standards and Technology (NIST) is providing research under an Interagency Agreement. Neither the NRC nor NIST are signatories to the CRADA.

The periods of cementitious performance being evaluated are up to and >100 years for operating facilities and > 1000 years for waste management. The set of simulation tools and data developed under this project will be used to evaluate and predict the behavior of cementitious barriers used in near-surface engineered waste disposal systems, e.g., wasteforms, containment structures, entombments, and environmental remediation, including decontamination and decommissioning analysis of structural concrete components of nuclear facilities (spent-fuel pools, dry spent-fuel storage units, and recycling facilities such as fuel fabrication, separations processes). Simulation parameters will be obtained from prior literature and will be experimentally measured under this project, as necessary, to demonstrate application of the simulation tools for three prototype applications (wasteform in concrete vault, high-level waste tank grouting, and spent-fuel pool). Test methods and data needs to support use of the simulation tools for future applications will be defined.

The CBP project is a multi-year effort focused on reducing the uncertainties of current methodologies for assessing cementitious barrier performance and increasing the consistency and transparency of the assessment process. The results of this project will enable improved risk-informed, performance-based decision-making and support several of the strategic initiatives in the DOE Office of Environmental Management Engineering & Technology Roadmap. Those strategic initiatives include 1) enhanced tank closure processes; 2) enhanced stabilization technologies; 3) advanced predictive capabilities; 4) enhanced remediation methods; 5) adapted technologies for site-specific and complex-wide D&D applications; 6) improved SNF storage, stabilization and disposal preparation; 7) enhanced storage, monitoring and stabilization systems; and 8) enhanced long-term performance evaluation and monitoring.
CEMENTITIOUS BARRIERS PARTNERSHIP
2015 MID-YEAR STATUS REPORT

SUMMARY
The DOE-EM Office of Tank Waste Management Cementitious Barriers Partnership (CBP) is chartered with providing the technical basis for implementing cement-based waste forms and radioactive waste containment structures for long-term disposal. Therefore, the CBP ultimate purpose is to support progress in final treatment and disposal of legacy waste and closure of High-Level Waste (HLW) tanks in the DOE complex. This status report highlights the CBP 2015 Software and Experimental Program efforts and accomplishments that support DOE needs in environmental cleanup and waste disposal. DOE needs in this area include:

- Long-term performance predictions to provide credibility (i.e., a defensible technical basis) for regulator and DOE review and approvals,
- Facility flow sheet development/enhancements, and
- Conceptual designs for new disposal facilities.

In 2015, the CBP plans to release its newest version, the CBP Software Toolbox – “Version 3.0”, which will include new STADIUM carbonation and damage models, a new SRNL module for transport properties and flow in fractured and in-tact cementitious materials, and a new LeachXS/ORCHESTRA (LXO) oxidation module. In addition, improved STADIUM sulfate attack and chloride models will be included. This is in addition to the LXO modules for sulfate attack, carbonation, constituent leaching, and percolation with radial diffusion (for leaching and transport in cracked cementitious materials), of which will also be improved for Version 3.0. These STADIUM and LXO models are applicable and can be used by both DOE and the Nuclear Regulatory Commission (NRC) for service life and long-term performance evaluations and predictions of nuclear and radioactive waste containment structures across the DOE complex.

In 2015, the Cementitious Barriers Partnership is providing tangible progress toward fulfilling the objective of developing a set of software tools and experimental programs to improve understanding and prediction of the long-term structural, hydraulic and chemical performance of cementitious barriers used in nuclear applications. To reflect this progress, CBP partners authored and are currently drafting many reports including six papers that were presented at WM2015:

- **The Cementitious Barriers Partnership Experimental Programs and Software Advancing DOE’s Waste Disposal/Tank Closure Efforts – 15436**: Heather Burns, Greg Flach, Frank Smith, Christine Langton, Savannah River National Laboratory (SRNL), Savannah River Site (SRS), Aiken, SC; Kevin Brown, David Kosson, Vanderbilt University, Dept. of Civil and Environmental Engineering, Nashville, TN; Eric Samson, SIMCO Technologies, Inc.; Pramod Mallick, US DOE.

- **Characterization of Unsaturated Hydraulic Conductivity in Fractured Media Using the Multistep Outflow Method - 15461**: Greg Flach, Ken Dixon, and Ralph Nichols, Savannah
River National Laboratory, Savannah River Site, Aiken, SC.

- **Reactive Transport Modeling and Characterization of Concrete Materials with Fly Ash Replacement under Carbonation Attack – 15477**: J. L. Branch, K. G. Brown, and D. S. Kosson, Vanderbilt University, Dept. of Civil and Environmental Engineering, Nashville, TN; J. R. Arnold, NIST, 100 Bureau Drive, Stop 1070, Gaithersburg, MD; and H. A. van der Sloot, Hans van der Sloot Consultancy, Langedijk, The Netherlands.

- **X-Ray Diffraction of Slag-based Sodium Salt Waste Forms – 15513**: C. A. Langton and D. M. Missimer, Savannah River National Laboratory, Savannah River Site, Aiken, SC.

- **Tc Oxidation in Slag-Based Sodium Salt Waste forms Exposed to Water and Moist Hanford Soil – 15514**: C. A. Langton, Savannah River National Laboratory, Savannah River Site, Aiken, SC.

- **Demonstrating Integration of CBP and ASCEM Simulation Tools – 15627**: Pramod Mallick, Justin Marble, Patricia Lee, US DOE; Greg Flach, Heather Burns, Roger Seitz, Savannah River National Laboratory, Savannah River Site, Aiken, SC; Paul Dixon, Los Alamos National Laboratory.

**FY2015 CBP Experimental Studies Overview**

In 2015, the CBP experimental programs are continuing to have a significant impact on the DOE complex by providing specific data unique to DOE sodium salt wastes at both Hanford and SRS which are not readily available in the literature. The programs are designed to produce significant data shedding light on the performance of the concretes selected for disposal of DOE salt waste forms at SRS. Experimental programs on technetium (Tc) mobility, cement phase characterization of damaged cementitious materials, and concrete performance after exposure to aggressive solutions are anticipated to have a significant impact to improve the understanding of the performance DOE cementitious barriers. The experimental studies listed below are summarized in this report.

I. Tc Mobility – Measurement of Oxidation Front in Cementitious Materials (SRNL)
II. Damaged CBP Cementitious Material Phase Characterization (SRNL)
III. Measurement of Hydraulic Conductivity in Fractured Materials (Method Development) – (SRNL)
IV. Durability of DOE Cementitious Material under Aggressive Solutions (SIMCO)
V. Transport Properties Measurement (SIMCO)
VI. Effect of damage on transport properties of concrete (SIMCO)
FY2015 CBP Software Development Overview

In 2015, the CBP plans to release its new Software Toolbox - Version 3.0, a software package providing new concrete degradation models that assist in lifetime predictions for cementitious structures. The CBP experimentally-based software Toolbox will include new and improved software modules used to predict degradation depths and damage due to sulfate attack, chloride attack, and carbonation for DOE cementitious waste structures. The CBP also plans to provide a QA software package to assist DOE users in qualifying the use of the software. The CBP also plans to conduct an integrated demonstration of ASCEM and CBP Software in 2015 after the software development is completed.

I. New CBP Software “Version 3.0” Development

- SRNL
  - Fractured Property and Flow Data Base

- SIMCO Technologies, Inc. (SIMCO)
  - Sulfate Attack Upgrades
  - Damage Module
  - Chloride Module
  - Carbonation Module

- Vanderbilt University
  - Oxidation Module

II. Improved Software QA Documentation for CBP Software

III. Integrated Demonstration of CBP/ASCEM Software

FY2015 CBP EXPERIMENTAL STUDIES

The CBP provides great value to the DOE complex through the development of the experimentally-based simulation tools that model important degradation mechanisms much needed for technical support of the DOE facility PAs. The experimental programs, in addition to providing data for calibration and validation of the CBP software tools, provide support directly to future DOE facility flowsheets and design. Applying understanding through experimental efforts to simulation tools and facility design is a necessary need in the DOE complex.

In FY2015, CBP experimental efforts have focused on the following DOE areas of interest:

- Technetium (Tc) Mobility,
- Characterization of damaged cementitious materials to understand and identify degradation mechanisms,
- Measurement of key transport properties in cementitious materials (method development), and
- Exposure of DOE cementitious barrier materials under various exposure conditions and measurement of the resultant properties.

The significance and deliverables as well as status for these efforts are shown in Table 1.

Table 1: CBP Experimental Program and Significance

<table>
<thead>
<tr>
<th>CBP Partner</th>
<th>Experimental Program</th>
<th>Significance</th>
<th>Deliverable/Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRNL</td>
<td>Tc Mobility – In Different Exposure Conditions</td>
<td>SRNL testing has shown that Tc mobility is most influenced by exposure to oxygen (via the oxidation front). This work involves exposing DOE salt-based waste forms to various conditions in water and Hanford soils to better understand the impact to Tc mobility.</td>
<td>FY2015 Report issued.</td>
</tr>
<tr>
<td></td>
<td>Tc Mobility – Oxidation Rate Measurement Development</td>
<td>This work involves development of a method to measure the oxygen diffusion rate through cementitious material to better understand the impact to Tc mobility.</td>
<td>FY2015 Report/Experimental test equipment is procured and test set-up complete. Initial testing in April 2015.</td>
</tr>
<tr>
<td></td>
<td>Characterization of Sodium based Salt Waste Forms and Damaged Cementitious Barrier Waste Forms</td>
<td>Characterization of sodium based salt waste forms is complete and FY2015 report has been issued. Damaged CBP Samples of Concrete Barriers from SIMCO Exposure Testing will be characterized with XRD and SEM to understand and identify the degradation mechanisms. Results of the mineral assemblage can then be incorporated into CBP models to significantly impact the results.</td>
<td>FY2015 Report/Damaged CBP samples received from SIMCO. XRD of samples has been initiated.</td>
</tr>
<tr>
<td></td>
<td>Measurement of Hydraulic Conductivity of Fractured Cementitious Materials (CM)</td>
<td>Methods exist for in-tact cementitious materials but not fractured. SRNL is developing a method to measure hydraulic conductivity in fractured materials. Considered “cutting edge” of technology to provide for fractured materials.</td>
<td>FY2015 Report/Report has been drafted and internally reviewed.</td>
</tr>
<tr>
<td>SIMCO</td>
<td>Exposure of Cementitious</td>
<td>Phase I experimental results showed that damage does not occur in high pH solutions</td>
<td>Report/ Report drafted, reviewed,</td>
</tr>
</tbody>
</table>
SRNL Technetium (Tc) Mobility Studies

- In Slag-Based Sodium Salt Waste forms Exposed to Water and Moist Hanford Soil (FY2015 SRNL Report Issued)

Several U.S. DOE sites use or plan to use waste forms and/or concrete containment structures for radioactive waste disposal that are designed to have a chemically reducing environment to immobilize selected contaminants such as Tc(VII)O$_4^-$ and Cr(VI)O$_4^{2-}$. These waste forms and containment structures are typically deployed in near surface unsaturated oxidizing environments. Consequently, the effect of exposure to air (oxygen) and water containing dissolved oxygen during production, during the period of institutional control, and over the long term period of performance is important for predicting the speciation and mobility of the redox sensitive radioactive and stable contaminants. An understanding of factors that affect the oxidation state of redox sensitive contaminants stabilized in cementitious waste forms is required to improve waste forms and engineered barriers for shallow land disposal. In
addition, the parameters and relationships for the 1) rate of bulk matrix oxidation and 2) potential for and efficiency of re-reduction of soluble Tc in cured un-oxidized portions of waste forms are required for predicting long-term performance.

The rate of oxidation is important to the long-term performance of reducing salt waste forms because the solubility of some contaminants, e.g., technetium, is a function of oxidation state. TcO$_4^-$ in the salt solution is reduced to Tc(IV) and has been shown to react with ingredients in the waste form to precipitate low solubility sulfide and/or oxide phases. Upon exposure to oxygen, the compounds containing Tc(IV) oxidize to the pertechnetate ion, Tc(VII)O$_4^-$, which is highly soluble in water and aqueous solutions. Consequently, the rate of technetium oxidation front advancement into a monolith and the technetium leaching profile as a function of depth from an exposed surface are important to waste form performance and ground water concentration predictions. The rate of oxidation front advancement into a monolith and the effect of oxygen ingress on redox sensitive contaminants are needed to:

1) Develop the conceptual model for performance predictions,
2) Provide data to parameterize fate and transport models, and
3) Validate computational codes.

A method for measuring contaminant oxidation fronts for redox sensitive contaminants in cementitious waste forms containing GGBFS was recently developed at the Savannah River National Laboratory (SRNL). This method is based upon leaching depth-discrete subsamples obtained as a function of distance from an exposed surface. Leaching is performed in a zero head space container using deionized, de-aerated water to minimize oxidation during the leaching process. Leaching time was 48 ± 4 hours.

The objectives of this study were to: utilize depth-discrete sampling and zero head space leaching to explore the effect of exposing cured waste forms to moist soil and DI water in a 1-D experimental configuration. More specifically, the effect of these exposure conditions on Tc leachability as a function of distance from the exposed surface was determined.

• Measurement of Oxidation Rate (Method Development)

Experiments to measure the rate of oxygen transport through cement waste forms, especially waste forms that chemically reduce certain contaminants such as Tc(VII), were initiated. A diffusion chamber was designed and fabricated for gas diffusion measurements (Figure 1). Several oxygen sensing methods were identified and incorporated in the experimental design. Initial leak testing of the gaseous diffusion cell was successfully completed and measurements have begun on a cement waste form trial sample. A test plan is being prepared for a series of experiments to measure non-reactive transport through materials with a range of water saturations. A follow on test plan for reactive oxygen transport is also in the planning stage.
Cementitious materials are used to solidify and stabilize aqueous based radioactive waste containing sodium salts. The types and proportions of cementitious ingredients used to treat aqueous radioactive waste streams containing sodium salts depend on the performance objectives for the waste forms and the compositions of the waste streams. Matrix phases can stabilize certain contaminants (co-precipitation, substitution, ion exchange, and/or sorption), influence processing properties, and are responsible for physical properties and durability of the cured waste forms. Consequently, characterization of the matrix (binder) mineralogy (chemical compositions and crystalline/non-crystalline structures) is important for predicting contaminant leaching and evolution of the materials as a function of time and changing conditions.

At the present time, the matrices of these cementitious waste forms are not well characterized because a large portion of the matrix is made up of phases that have poorly ordered structures and form solid solutions involving cation and anion substitutions. In
addition, the matrix consists of micrometer and sub-micrometer particles intergrown to the extent that individual particles are difficult to characterize using scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX).

SRNL conducted an experimental program characterizing a series of DOE sodium salt-based waste forms using x-ray diffraction last year. Characterization of the matrix mineralogy is important for predicting contaminant leaching and evolution of the materials as a function of time and changing conditions. The objective of this study was to provide initial phase characterization for the cementitious salt waste form.

A report has been published in FY2015 on the results of the mineral phase characterization of DOE salt-based waste forms. The objective of this report was to characterize the phase assemblages in the Cementitious Barriers Partnership reference case sodium salt waste form [Langton, 2009]. This information can be used to: 1) generate a baseline for the evolution of the waste form as a function of time and conditions, 2) design new binders based on matrix mineralogy, 3) understand and predict anion and cation leaching behavior of contaminants of concern, and 4) predict performance of the waste forms and 5) identify appropriate phase solubility and thermodynamic data. Characterization of the mineralogy is also important for understanding the buffering effects that the waste form has on infiltrating water/leachates.

**CBP Damaged DOE Cementitious Barrier Materials**

In FY2015, SRNL is continuing the characterization work on CBP materials, however, this time for damaged CBP cementitious materials from SIMCO testing under aggressive solutions. SRNL will utilize both XRD and SEM to characterize the phases and understand the mineral assemblage and to better determine the mechanism that initiated the degradation. Samples from SIMCO have been received (Figure XXX) and a paper will be published in FY2015. This information can be used to: 1) generate a baseline for the evolution of the waste form as a function of time and conditions, 2) design new binders based on mineralogy of the binder, 3) understand and predict anion and cation leaching behavior of contaminants of concern, and 4) predict performance of the waste forms for which phase solubility and thermodynamic data are available. A report will be published in FY2015 on the results of the mineral phase characterization of cementitious barrier materials.
SRNL Hydraulic Conductivity Method Development in Fractured Cementitious Materials

In FY2015, SRNL continued the CBP experimental program on the method development for measuring hydraulic conductivity in fractured cementitious materials which is a key transport property used in DOE performance assessments. DOE Performance Assessments often involve cementitious barriers and/or waste forms that are predicted or assumed to degrade over time due to various mechanisms such as carbonation-influenced reinforcing steel corrosion, external sulfate attack, differential settlement, and seismic activity. Physical degradation typically takes the form of small-scale cracking / fracturing, and the affected materials reside in unsaturated hydrogeologic zones. In these cases, unsaturated hydraulic properties are needed for fractured cementitious materials to simulate moisture movement and contaminant transport within and around the facility. The outflow extraction method has been developed to provide a suitable method for estimating these material properties.

SRNL will release a report in FY2015 describing the experimental program on the outflow extraction method apparatus and procedure (Figure 3), adapted for use with fractured media to measure the unsaturated hydraulic conductivity. The report documents results of the measurement of three micro-fractured grout specimens (Figure 4) through inverse modeling with HYDRUS-1D. The estimated hydraulic curves generally conform to expectations and appear to be reproducible based on repeat testing and similar results being achieved for similar fracture networks. These observations suggest that the outflow extraction method is a viable technique for characterizing the unsaturated hydraulic conductivity of micro-fractured cementitious materials. However, further testing is needed to provide rigorous method validation to confirm this tentative conclusion. With respect to PA applications, comparisons of the unsaturated conductivity for the micro-fractured grout samples
suggests that soils may serve as conservative surrogates for damaged cementitious materials, assuming that higher conductivity at higher tension heads is conservative for facility performance.

Fig. 3. Experimental apparatus for outflow extraction method.

Fig. 4. Radiography image showing fracture network in TR437 at 25% depth from the top surface.
SIMCO Exposure of DOE Barriers to Aggressive Solutions Experimental Study (Phase I and II)

The SIMCO Technologies, Inc. (SIMCO) experimental work aimed at supporting the assessment of long-term durability of concrete barriers containing sulfate-bearing salt wasteforms, present at both SRS and Hanford. SIMCO had conducted a two phase study with surprising results in the second phase study. Phase I experimental results showed that damage does not occur in high pH solutions in the presence of sulfate. A possible explanation for this is the absence of gypsum formation at high pH. SIMCO concluded that, although these results need further confirmation, they indicate that the high sulfate content found in the wasteform pore solution will not necessarily lead to severe damage to concrete typical of that used in SRS Saltstone Disposal Units 1/4.

SIMCO conducted additional experimental studies with contact solutions that examine limit cases useful for understanding the interaction between waste form pore solutions and the new SDU units (i.e., SDU 2) in Phase II. The scope was extended to hydrated cement pastes incorporating supplementary cementitious materials (SCM) such as fly ash and ground granulated blast furnace slag (GGBFS) that is characteristic of DOE cementitious barrier materials. Two paste mixes were equivalent to Vault 1/4 and SDU 2 concrete mixes uses at SRS in storage structures. Five different solutions, some of which incorporated high levels of carbonate and nitrate, were placed in contact with four different hydrated cement paste mixes. In all solutions, 150 mmol/L of SO$_4^{2-}$ (14, 400 ppm) were present. The solutions included different pH conditions and different sodium content.

Globally, results were in line with the previous study and confirmed that high-pH may limit the formation of some deleterious phases like gypsum. In this case, ettringite may form but is not necessarily associated with damage. However, the high concentration of sodium may be associated with the formation of an AFm-like mineral called U-phase.

The most significant evidences of damage were all associated with the Vault 2 paste analog (Figure XX1). This material proved very sensitive to high-pH. All measurement techniques used to monitor and evaluate damage to samples indicated significant alterations to this mix when immersed in contact solutions containing sodium hydroxide. It was hypothesized that the low cement content, combined with high silica content coming from silica fume, fly ash and GGBFS led to the presence unreacted silica. It is hypothesized that the pozzolanic reaction of these SCMs could not be activated due to the low alkali content, a direct consequence of low cement content. In this scenario, the material end up having a lot of silica available to react upon contact with sodium hydroxide, possibly forming a gel that may be similar to the gel formed in alkali-silica reactions. This scenario needs further experimental confirmation but it may explain the poor behavior of mix PV2 in presence of NaOH.
SIMCO Transport Properties Measurements

The mixtures were designed at the Savannah River National Laboratory and are identified as follow:

- Vault 1/4 concrete: w/b ratio of 0.38, prepared with ASTM Type I/II cement and slag;
- Vault 2 concrete: w/b ratio of 0.38, prepared with ASTM Type V cement, slag, fly ash, and silica fume.

Both mixtures were prepared with approximately 425 kg of binder. All raw materials were shipped to SIMCO Technologies’ laboratory, where the batches were prepared and the samples tested.

The testing protocol mostly focused on determining the transport properties of the mixtures. It was based on test methods developed by SIMCO. The same tests are incorporated in the protocol developed by the US Department of Defense and described in the Unified Facilities Guide Specifications (UFGS – 03 31 29) for new marine concrete construction, issued in August 2012. The tests yield parameters that can directly be incorporated in STADIUM®, a reactive transport model dedicated to the prediction of chemical alteration sustained by cement-based materials in aggressive environments. STADIUM® is a proprietary code developed by SIMCO and is part of the CBP Toolbox. The following transport properties were evaluated:

- Volume of permeable voids (porosity), in accordance with the ASTM C642 standard procedure: Standard Test Method for Density, Absorption and Voids in Hardened Concrete,
- Diffusion coefficients, on the basis of migration test results, which is a modified version of the ASTM C1202 procedure: Standard Test Method for Electrical Indication of Concrete’s Ability to Resist Chloride Ion Penetration,
- Water permeability, on the basis of drying test results, in accordance with ASTM WK37029: Measurement of Mass Loss Versus Time for One-Dimensional Drying of Saturated Concretes.
Tests were performed after different curing durations. In order to obtain data on the statistical distribution of transport properties, the measurements after 2 years of curing were performed on 10+ samples.

Overall, both mixtures exhibited very low tortuosities and permeabilities, a direct consequence of their low water-to-binder ratio and the use of supplementary cementitious materials. The data generated on 2-year old samples showed that porosity, tortuosity and permeability follow a normal distribution.

**SIMCO Effect of Damage on Transport Properties**

The objective of this experimental study was to provide experimental data relating damage in cementitious materials to changes in transport properties, which can eventually be used to support predictive model development.

In order to get results within a reasonable timeframe and to induce as much as possible uniform damage level in materials, concrete samples were exposed to freezing and thawing (F/T) cycles. The methodology consisted in exposing samples to F/T cycles and monitoring damage level with ultrasonic pulse velocity measurements. Upon reaching pre-selected damage levels, samples were tested to evaluate changes in transport properties.

Material selection for the study was motivated by the need to get results rapidly, in order to assess the relevance of the methodology. Consequently, samples already available at SIMCO from past studies were used. They consisted in three different concrete mixtures cured for five years in wet conditions. The mixtures had water-to-cement ratios of 0.5, 0.65 and 0.75 and were prepared with ASTM Type I cement only.

The results showed that porosity is not a good indicator for damage caused by the formation of microcracks. Some materials exhibited little variations in porosity even for high damage levels. On the other hand, significant variations in tortuosity were measured in all materials. This implies that damage caused by internal pressure do not necessarily creates additional pore space in the microstructure but likely creates new thin pathways between existing pore space for species to travel.

**SIMCO Damage of Concrete Exposed to Wasteform Material**

The objective of this experimental study was to provide data from an actual Saltstone/concrete system, prepared in the lab maintained in a controlled environment. Saltstone slurry was cast over Vault 1/4 and Vault 2 concrete samples. The concrete mixtures were characterized in a previous stage of the ongoing experimental program performed at SIMCO. The setup is illustrated on Figure 6.
The experiment started in 2013. The 2-year duration was reached in the first half of FY2015. At the time of preparing the mid-year report for FY15, the analysis was still ongoing. Early results showed that the presence of sulfate in the wasteform led to the formation of ettringite in the concrete substrate (Figure 6).

![Fig. 6. Setup for the Saltstone/concrete study](image)

Vanderbilt University Experimental Programs - Reactive Transport Modeling and Characterization of Concrete Materials with Fly Ash Replacement under Carbonation Attack

There are various degradation methods that can affect the integrity of these materials over this time frame including carbonation which lowers the alkalinity of the material that can lead to cracking in materials with steel reinforcement. The rate and extent of carbonation in these materials can be impacted by the addition of fly ash and the fly ash source. To characterize the carbonation reaction, changes in the microstructure and elemental distribution as a function of extent of carbonation and fly ash type are being evaluated using scanning electron microscopy (SEM) coupled with energy dispersive x-ray spectroscopy (EDS). The migration and deposition of chemical species were observed in carbonated regions from EDS data, which are attributed to changes in alkalinity and solubility as determined from EPA Method 1313 (Liquid-solid partitioning (LSP) as a function of eluate...
pH). Changes in mass transport properties resulting from carbonation were observed using EPA Method 1315 (Mass transfer rates in monolithic and compacted granular materials using semi-dynamic tank leaching procedures). Carbonation reactions in each material were simulated using LeachXS/ORCHESTRA, a reactive transport modeling tool, to provide further evidence of localized deposition and migration of chemical species due to changes in speciation and solubility.

**FY2015 CBP SOFTWARE DEVELOPMENT**

**I. New CBP Software “Version 3.0” Development**

The CBP Software Toolbox is a suite of software tools for simulating reactive transport in cementitious materials and certain important degradation phenomena. The primary software components are STADIUM, LeachXS/ORCHESTRA (LXO), and a GoldSim interface for probabilistic analysis of selected degradation scenarios. The current version released in 2014, “Version 2.0”, supports analysis of external sulfate attack, carbonation degradation analysis, chloride attack, and dual regime modeling for fractured and in-tact cementitious materials. Version 3.0 will include a new LeachXS/ORCHESTRA oxidation module, an upgraded STADIUM sulfate and chloride attack module, and a new STADIUM carbonation module and damage module. The integrated software for the Version 3.0 release is shown in Figure 8.
SRNL recognized the need of a materials property database of transport properties for both fractured and in-tact cementitious materials in addition to a tool for simulating the flow properties through degraded cementitious materials. Software development began in FY2014 and is being completed in FY2015 for the development of this new software module designated as FLOExcel. FLOExcel incorporates a uniform database and flow simulator to capture experimental data and simulate transport flow through both fractured and intact cementitious materials. The software module includes hydraulic parameters for both fractured and intact cementitious materials in the database and a standalone GoldSim framework to manipulate the data. The database will be updated with new data as it comes available. The software module will later be integrated into the new release of the CBP Toolbox, Version 3.0. A report has been recently drafted and internally reviewed and will be released in FY2015 describing the development of the FLOExcel package that includes:

1) A uniform database to capture CBP data for cementitious materials including their hydraulic properties.

Fig. 8. CBP Software Version 3.0

SRNL - Fractured Property and Flow Data Base
2) A Software and GoldSim User Interface to calculate hydraulic flow properties of degraded and fractured cementitious materials.

SIMCO Technologies, Inc. (SIMCO)

- Sulfate Attack Damage Model: In parallel with the experimental program, SIMCO continued the development of the damage model to be coupled with the sulfate ingress model. The model is based on the alteration of the pore size distribution following the local formation or dissolution of minerals in concrete exposed to aggressive environments.

This approach needed the development of a new calculation module to predict the composition of mineral phases in hydrated cement pastes, in presence of supplementary cementitious materials such as fly ash or ground granulated blast furnace slag. Compared to the previous methodology developed by SIMCO, the new module improved the prediction of iron-based hydrates and now accounts for magnesium in cement and admixtures.

A prototype model was completed in the first-half of FY2015. The implementation of the model in the STADIUM platform will be completed in the second-half of 2015.

- Chloride Model: a chloride ingress model was already included in STADIUM when the CBP project started. The model was improved recently, in part because of the improvements to the mineral phase calculation module, as described previously. The new model better accounts for the impact of iron-based AFm phases on chloride binding in concrete. This improves the reliability of the prediction of corrosion initiation of steel rebars in concrete mixes exposed to chloride-laden environments.

- Carbonation Module: the impact of the presence of carbonates in groundwater on concrete can be accounted for in STADIUM. Species and minerals were added to STADIUM chemical database. The model predicts for instance the formation of calcite and carbonate-AFm phases upon carbonate ingress, along with the corresponding pH drop in the material and dissolution of portlandite resulting from the formation of calcite. These functionalities will be fully integrated in the STADIUM software platform in the second-half of FY2015.

LeachXS/ORCHESTRA (LXO) Oxidation Module

- Oxidation Module: Certain redox-sensitive species (e.g., Tc-99) drive long-term risks for waste disposal at major DOE Sites, including both Hanford and Savannah River. For example, Tc-99 becomes mobile in the environment when oxidized and thus understanding the redox behavior of important constituents in cementitious wasteforms and other materials. A source-term model including chemical speciation and redox effects is being developed for cementitious materials to describe both Saltstone (SRS) and Cast Stone (Hanford).

- Existing Modules: Improvements will be made to both the existing Carbonation Module
(based on experimental results described above) and Percolation with Radial Diffusion Module.

**Improved Software QA Documentation for CBP Software**

CBP Software has been used in recent performance assessment analysis for DOE cement barriers and end-users have communicated the need for improved software QA documentation that more easily help them meet their site QA requirements. The CBP Partners are actively responding to this request by initiating an effort to provide more comprehensive software QA documentation that satisfies the graded requirements of DOE 414.1D and NQA-1 requirements for the expected uses of the CBP products (e.g., performance assessments). The intent of this effort is that end-users can be confident in the quality of the CBP software and easily leverage CBP documentation to satisfy their site-specific software QA requirements, verify the validity of their local installation, and readily identify software configurations associated with chronological events (e.g., releases, workshops).

**CBP/ASCEM Integrated Software Demonstration**

The DOE-EM Advanced Simulation Capability for Environmental Management (ASCEM) and Cementitious Barriers Partnership (CBP) programs are producing software for end-users involved with environmental cleanup and waste disposal. Although both software products nominally simulate porous-medium flow and solute transport, the scope and emphasis of ASCEM and the CBP are substantially different. Specialized CBP software capabilities for simulating reactive transport in cementitious materials will be utilized in a near-field simulation of radionuclide leaching from the engineered system (i.e., the waste tank). The high-performance computing (HPC) capabilities of the ASCEM Amanzi simulator will be utilized to simulate far-field flow and transport. The ASCEM flow simulation will provide boundary conditions to the CBP near-field model, which in turn will provide radionuclide source terms to the ASCEM far-field transport simulation as shown in Figure 9.

![Fig. 9. Integrated ASCEM and CBP Software](image)

**Fig. 9. Integrated ASCEM and CBP Software**
The purpose of the joint analysis is to demonstrate specialized CBP capabilities for simulating reactive transport in cementitious materials, and ASCEM reactive transport capabilities (cement/waste form leachate impacted in far-field soil), and guide ASCEM and CBP development of interfaces to external codes and information. The CBP is a project of coordinated software development and experimentation focused on cementitious materials. ASCEM is a complementary project aimed at developing next-generation, science-based, reactive flow and transport simulation capabilities and supporting modeling toolsets within a high-performance computing framework to address DOE-EM’s waste management and environmental cleanup challenges.

Figure 10 provides another view of how the two crosscutting projects can be used in a complementary manner to enhance the DOE-EM PA and risk assessment. Specialized CBP capabilities for simulating reactive transport in cementitious materials can be utilized in a near-field simulation of radionuclide leaching from the engineered system such as landfills, liquid waste tanks or disposal trenches. As illustrated in Figure X, closure of a representative liquid waste tank includes grouting the residual waste and the empty spaces in the tank. The CBP near-field model domain will encompass the reducing cementitious grout in the tank, the steel tank liner, the concrete tank wall or shell, and a sufficient amount of adjoining soil (approximately 1 m thickness) to adequately capture significant leachate interactions between the concrete wall and soil. The high-performance computing capabilities of the ASCEM Amanzi simulator can be utilized to simulate far-field flow and transport in the natural environment outside the closed tank. The joint demonstration illustrates how two crosscutting projects can be used in a complementary manner to enhance DOE-EM PA and risk assessment. A report will be published in FY2015 describing the specifics of a representative DOE waste tank.
CBP WM2015 REPORT ABSTRACTS

The Cementitious Barriers Partnership Experimental Programs and Software Advancing DOE’s Waste Disposal/Tank Closure Efforts – 15436: Heather Burns, Greg Flach, Frank Smith, Christine Langton, Savannah River National Laboratory (SRNL), Savannah River Site (SRS), Aiken, SC; Kevin Brown, David Kosson, Vanderbilt University, Dept. of Civil and Environmental Engineering, Nashville, TN; Eric Samson, SIMCO Technologies, Inc.; Pramod Mallick, US DOE.

The U.S. Department of Energy Environmental Management (DOE-EM) Office of Tank Waste Management sponsored Cementitious Barriers Partnership (CBP) is chartered with providing the technical basis for implementing cement-based waste forms and radioactive waste containment structures for long-term disposal. DOE needs in this area include the following to support progress in final treatment and disposal of legacy waste and closure of High-Level Waste (HLW) tanks in the DOE complex:

- Long-term performance predictions and
- Flow sheet development and flow sheet enhancements
- Conceptual designs for new disposal facilities

The DOE-EM Cementitious Barriers Partnership is producing software and experimental programs resulting in new methods and data needed for end-users involved with environmental cleanup and waste disposal. Both the modeling tools and the experimental data have already benefited the DOE sites in the areas of performance assessments by increasing confidence backed up with modeling support, leaching methods, and transport properties developed for actual DOE materials. In 2014, the CBP Partnership released the CBP Software Toolbox – “Version 2.0” which provides concrete degradation models for: 1) sulfate attack, 2) carbonation, 3) chloride initiated rebar corrosion, and includes constituent leaching. These models are applicable and can be used by both DOE and the Nuclear Regulatory Commission (NRC) for service life and long-term performance evaluations and predictions of nuclear and radioactive waste containment structures across the DOE complex (Figure 11) including:

![Tank Closure](image1) ![Saltstone Disposal](image2) ![Low Level Waste Vault Grouted](image3)

Fig. 11. Various DOE Cementitious Barriers in Waste Management
- Future SRS Saltstone and HLW tank performance assessments and special analyses
- Hanford site HLW tank closure projects and other projects in which cementitious barriers are required
- The Advanced Simulation Capability for Environmental Management (ASCEM) project which requires source terms from cementitious containment structures as input to their flow simulations
- Regulatory reviews of DOE performance assessments
- Nuclear Regulatory Commission reviews of commercial nuclear power plant (NPP) structures which are part of the overall US Energy Security program to extend the service life of NPPs

In addition, the CBP experimental programs have had a significant impact on the DOE complex by providing specific data unique to DOE sodium salt wastes at Hanford and SRS which are not readily available in the literature. Two recent experimental programs on cementitious phase characterization and on technetium (Tc) mobility have provided significant conclusions as summarized below:

- Recent mineralogy characterization discussed in this paper illustrates that sodium salt waste form matrices are somewhat similar to but not the same as those found in blended cement matrices which to date have been used in long-term thermodynamic modeling and contaminant sequestration as a first approximation. Utilizing the CBP generated data in long-term performance predictions provides for a more defensible technical basis in performance evaluations.
- In addition, recent experimental studies related to technetium mobility indicate that conventional leaching protocols may not be conservative for direct disposal of Tc-containing waste forms in vadose zone environments. These results have the potential to influence the current Hanford supplemental waste treatment flow sheet and disposal conceptual design.

**Characterization of Unsaturated Hydraulic Conductivity in Fractured Media Using the Multistep Outflow Method – 15461** Greg Flach, Ken Dixon, and Ralph Nichols, Savannah River National Laboratory, Savannah River Site, Aiken, SC.

The multistep outflow method is routinely used to characterize the unsaturated hydraulic conductivity of soils. The technique involves placing a soil sample in a pressure plate apparatus, subjecting the sample to multiple gas pressures in discrete steps through time, and measuring the transient volume of pore fluid extracted. Unsaturated hydraulic property values are estimated through inverse modeling of the experimental conditions. In this study the multistep outflow concept was applied to micro-cracked cementitious materials to assess the efficacy of the technique for these materials. The cementitious materials tested were salt-waste simulant grout samples artificially damaged through oven-drying.
Compared to typical soils, fractured media exhibit higher saturated conductivity and lower air-entry pressure, and the volume of fluid extractable from fractures is much lower than soil porosity. To accommodate these material differences the standard test apparatus was modified to incorporate a higher conductivity ceramic pressure plate, a high-precision digital balance for logging outflow mass, a low volume (diameter) effluent line, multiple inline high-precision gas regulators, and a high-precision low-range pressure gauge. Testing to date indicates that the modified apparatus can provide a viable means to measure the unsaturated hydraulic properties of micro-fractured cementitious materials. However the accuracy/unicity of inverse modeling is limited by the inherent characteristics of fractured media: high saturated conductivity, low air-entry pressure, and strong non-linearities. Hydraulic property results in the form of van Genuchten / Mualem curves are presented for three fractured grout specimens.

DOE Performance Assessments often involve cementitious barriers and/or waste forms that are predicted or assumed to degrade over time due to various mechanisms such as carbonation-influenced reinforcing steel corrosion, external sulfate attack, differential settlement, and seismic activity. Physical degradation typically takes the form of small-scale cracking / fracturing, and the affected materials reside in unsaturated hydrogeologic zones. In these cases, unsaturated hydraulic properties are needed for fractured cementitious materials to simulate moisture movement and contaminant transport within and around the facility. The outflow extraction method, as implemented in the present study, provides a suitable method for estimating these material properties.

Reactive Transport Modeling and Characterization of Concrete Materials with Fly Ash Replacement under Carbonation Attack – 15477: J. L. Branch, K. G. Brown, and D. S. Kosson, Vanderbilt University, Dept. of Civil and Environmental Engineering, Nashville, TN; J. R. Arnold, NIST, 100 Bureau Drive, Stop 1070, Gaithersburg, MD; and H. A. van der Sloot, Hans van der Sloot Consultancy, Langedijk, The Netherlands.

There currently lacks sufficient knowledge to accurately characterize structural, hydraulic, and chemical performance of cementitious materials that are required to contain and shield nuclear waste for thousands of years. There are a number of degradation methods that can affect the integrity of these materials over this time frame including carbonation which lowers the alkalinity of the material and can induce cracking in materials with steel reinforcement. The rate and extent of carbonation in these materials is impacted by the addition of fly ash and its composition which can vary depending on the fly ash source. To characterize the carbonation reaction, the changes in the microstructure and elemental distribution as a function of extent of carbonation and fly ash type were evaluated using scanning electron microscopy (SEM) coupled with energy dispersive x-ray spectroscopy (EDS). Microconcretes were prepared with no fly ash (control case) and with fly ash of various calcium compositions. The progression of the carbonation front was observed in the backscattered electron images by the formation of calcium carbonate and depth was confirmed with a phenolphthalein pH indicator test. The migration and deposition of chemical species were observed in carbonated regions from EDS data and were explained based on the changes in material alkalinity and solubility determined from EPA Method 1313 (Liquid-solid partitioning (LSP) as a function of eluate pH). The changes in mass transport properties from carbonation were observed
using EPA Method 1315 (Mass transfer rates in monolithic and compacted granular materials using semi-dynamic tank leaching procedures). The carbonation reaction in each material was simulated using LeachXS/ORCHESTRA, a reactive transport modeling tool, which provided further evidence of localized deposition and migration of chemical species due to changes in speciation and solubility.

**X-Ray Diffraction of Slag-based Sodium Salt Waste Forms – 15513** C. A. Langton and D. M. Missimer, Savannah River National Laboratory, Savannah River Site, Aiken, SC.

Cementitious materials are used to solidify and stabilize aqueous based radioactive waste containing sodium salts. The types and proportions of cementitious ingredients used to treat aqueous radioactive waste streams containing sodium salts depend on the performance objectives for the waste forms and the compositions of the waste streams. This paper documents sample preparation and x-ray diffraction results for a series of materials made with water or highly alkaline sodium salt simulated waste water and cementitious binders. The objective of this study was to: 1) generate a base line for the evolution of the waste form as a function of time and conditions, 2) design new binders based on mineralogy of the binder, 3) understand and predict anion and cation leaching behavior of contaminants of concern, and 4) predict performance of the waste forms for which phase solubility and thermodynamic data are available. Characterization of the mineralogy is also important for understanding the buffering effects that the waste form has on infiltrating water / leachates.

In summary, mixtures of Type II portland cement, Grade 100 ground granulated blast furnace slag (GGBFS) and carbon burn-out (CBO) Class F Fly ash which were hydrated with water contained hydrated phase assemblages typical of those reported in the literature. The calcium silicate hydrate phase assemblage in samples hydrated with the alkaline 4.4 M sodium salt simulated waste solution was found to be a function of the \((\text{CaO} + \text{MgO}) / (\text{SiO}_2 + \text{Al}_2\text{O}_3)\) ratio of the samples characterized. No significant differences were detected in samples cured 2 months and 14 months in sealed containers at ambient indoor temperatures.

Slag and a blend of slag and cement hydrated with caustic 4.4 M Na salt solution resulted in the most crystalline matrix. In addition to poorly ordered C-S-H, these samples contained fairly well ordered C-S-H I (a precursor of 14Å tobermorite) and 11 Å Al-substituted tobermorite. These crystalline C-S-H phases did not form or were present in only trace amounts in slag blends containing about 45 to 62 mass percent fly ash. These slag-Class F fly ash blends had a higher silica plus alumina content relative to lime and magnesia than the blends that produced C-S-H I and Al-substituted tobermorite. The calcium silicate binder in the 10:45:45 mixture of cement : slag : fly ash was made up of poorly ordered C-S-H. The sample cured for 14 months may contain a small amount of the more crystalline calcium silicate hydrate phases.

Layered double hydroxides in the hydrotalcite (magnesium-aluminum carbonate hydroxide) and hydrocalumite / AFm phases (calcium aluminum hydroxide) were present in mixtures containing slag. The specific phase(s) were not identified because these phases form solid solutions and have a
considerable amount of overlap in their x-ray patterns. Sodium nitrate was the only sodium salt phase identified in x-ray diffraction patterns of the samples hydrated with salt solution. Drying during x-ray diffraction sample preparation may have resulted in precipitation of the sodium nitrate or it may have been present in the samples prior to x-ray sample preparation. Sodium sulfate, aluminate, and carbonate may have been incorporated in the structures of the layered double hydroxide (AFm) type phases. These mixed metal layered double hydroxides make up an important fraction of the matrix in the slag containing blends hydrated with caustic salt solution. They are among the few oxide-based phases that exhibit substantial, permanent anion exchange capacity [Kirkpatrick, et al. 1999, Plamer, et al., 2009, and Zhang and Reardon, 2003]. They also contribute to the structural properties of cementitious matrices [Taylor, 1997].

**Tc Oxidation in Slag-Based Sodium Salt Waste forms Exposed to Water and Moist Hanford Soil – 15514** C. A. Langton, Savannah River National Laboratory, Savannah River Site, Aiken, SC.

Several U.S. DOE sites use or plan to use waste forms and/or concrete containment structures for radioactive waste disposal that are designed to have a chemically reducing environment to immobilize selected contaminants such as Tc(VII)O$_4^-$ and Cr(VI)O$_4^{2-}$. These waste forms and containment structures are typically deployed in near surface unsaturated oxidizing environments. Consequently, the effect of exposure to air (oxygen) and water containing dissolved oxygen during production, during the period of institutional control, and over the long term period of performance is important for predicting the speciation and mobility of the redox sensitive radioactive and stable contaminants.

Both the SRS and Hanford waste streams contain soluble technetium which may require stabilization to meet disposal requirements. Technetium stabilization is a difficult problem because: 1) Tc is soluble and very mobile in the oxidized form typical of near surface environments, and 2) Tc-99 is a long-lived isotope with a half-life of 2.1E+05 years which places demanding requirements on the engineered barriers and environment to meet current regulatory disposal requirements.

A depth-discrete sampling and leaching method approach for measuring contaminant oxidation rate (effective contaminant specific oxidation rate) was used in this study. The method was modified by coating all sides of a cylindrical sample with an impermeable epoxy and cutting a fresh surface 2 to 2.5 cm from the original top surface eliminates sample inhomogeneity as the result of settling as a reason from observed results and provides 1-D soluble ion transport and gas transport information.

Soluble Tc was leached from all of the depth-discrete subsamples from both Tc2-9 and Tc2-10 which strongly suggests that oxygen was present in the entire length of both samples. About 24 mass percent of the Tc in the original sample, was leached (soluble) from subsamples between 0.8 and 46 mm below the exposed surface of Tc2-9 (exposed to Hanford sediment). The same percent (24%) was leached from the subsamples between 0.8 and 11 mm below the exposed surface of Tc2-10 (exposed to DI water). This suggests that the rate of oxygen migration into the sample exposed to soil was faster than the rate of migration into the sample exposed to water which is consistent with the more rapid transport of ions through a gas phase as compared to a liquid phase. It is assumed
that moisture in the Hanford sediment was not sufficient to completely block the surface pores with respect to gas transport across the soil-waste form boundary. Based on nitrate leaching results for the depth-discrete subsamples, regions depleted in nitrates were identified from the top surfaces to 9.5 and 3 mm into samples Tc2-9 (exposed to moist Hanford sediment) and Tc2-10 (DI water). Low mass fractions of nitrate were leached from these depth-discrete samples compared to samples further from the exposed surface presumably because a significant portion of the nitrate had already migrated into the soil or water, respectively. Depth-discrete subsample leaching results for Na can be interpreted in the same way over the same regions in the two samples tested.

In conclusion, leaching monolithic porous cementitious waste forms in water appears to be conservative for non-redox sensitive contaminants. However, leaching data obtained under saturated exposure conditions do not appear to be conservative for redox sensitive contaminants which are easily oxidized. Leaching crushed samples in water still seems to be a conservative approach to estimating the concentrations of soluble contaminants in a waste form.

Demonstrating Integration of CBP and ASCEM Simulation Tools – 15627: Pramod Mallick, Justin Marble, Patricia Lee, US DOE; Greg Flach, Heather Burns, Roger Seitz, Savannah River National Laboratory, Savannah River Site, Aiken, SC; Paul Dixon, Los Alamos National Laboratory.

DOE-EM is supporting two crosscutting projects to develop software and conduct targeted experiments to enhance performance and risk assessment capabilities: the Cementitious Barriers Partnership (CBP) and the Advanced Simulation Capability for Environmental Management (ASCEM). The CBP is a smaller-scale project of coordinated software development and experimentation focused on cementitious materials. ASCEM is a larger-scale project aimed at developing next-generation, science-based, reactive flow and transport simulation capabilities and supporting modeling toolsets within a high-performance computing framework to address DOE-EM’s waste management and environmental cleanup challenges. Complementary integration of CBP and ASCEM software toolsets has been demonstrated through a joint simulation of radionuclide release and transport in a representative tank closure scenario. Specialized CBP capabilities for simulating reactive transport in cementitious materials were utilized in a near-field simulation of radionuclide leaching from the engineered system. The high-performance computing (HPC) capabilities of the ASCEM Amanzi simulator were utilized to simulate far-field flow and transport in the natural environment outside the closed tank. The ASCEM flow simulation provided boundary conditions to the CBP near-field model, which in turn provided radionuclide source terms to the ASCEM far-field transport simulation. The joint demonstration illustrates how the two crosscutting projects can be used in a complementary manner to enhance DOE performance and risk assessment.

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